

GRAVITY EFFECTS ON COMBUSTION SYNTHESIS OF GLASSES

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Abstract

The Combustion Synthesis technique has been used to produce glasses based on B_2O_3 - Al_2O_3 - MgO and CaO - Al_2O_3 . The combustion characteristics of these combustion synthesis reactions using both small cylindrical pellets (SCP) and large spherical pellets (LSP) are presented. Low density pellets (~35% of their theoretical density) were used, which made synthesis of low exothermic combustion reactions possible. Microstructural analysis of reacted samples was carried out to identify the glass-forming compositions.

The effects of gravity on the glass formation were studied aboard the KC-135 using SCP samples. Gravity seemed to have such obvious effects on the combustion characteristics that the wave velocity was lower and the width of the combustion wave was larger under reduced gravity conditions. Samples produced under low gravity also had more enhanced vitrification than those on ground, while some systems also exhibited lower combustion temperatures. It was also found that the container significantly affects both the combustion characteristics and microstructure. Substantially more devitrification occurred at the area which was in contact with the support (container).

Introduction

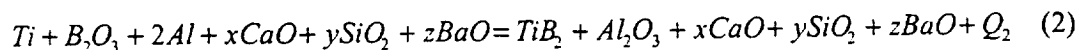
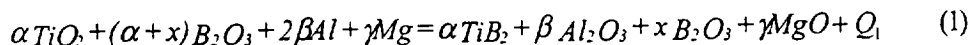
Microgravity offers a unique environment to study many scientific issues that are important to the glass industry. Since the gravity-driven phenomenon is absent, it promotes homogeneous nucleation and eliminates phase separations. Previous studies on the effects of gravity on the glass formation showed that gravity plays a significant role in the formation of high-quality glasses. Conducting glass synthesis under reduced gravity was found to reduce the immiscibility and reduce or eliminate devitrification of borderline composition glasses and, therefore, better glasses were formed. The information learned from these studies greatly enhanced our understanding of the role that gravity plays in glass formation, which undoubtedly will help create high-quality glasses under terrestrial conditions.

Traditional glass processing involves high temperature fusion of materials for a long period of time. On the other hand, the Self-propagating High Temperature Synthesis (SHS) or Combustion Synthesis technique is used in this work to produce glassy materials since the technique offers instant high combustion temperature without a furnace. Many high temperature crystalline materials have been produced by the SHS technique [1,2]. Recently, the technique has also been used to produce glasses [3-5].

Combustion Synthesis of two glass systems will be conducted on the International Space Station (ISS). This paper reports the combustion characteristics and microstructures of two glass systems produced by the Combustion Synthesis technique on ground and the gravity effects learned from the KC-135 flights.

Experimental Method

Two glass systems, B_2O_3 - Al_2O_3 - MgO and CaO - Al_2O_3 - SiO_2 - BaO were produced by the following combustion reactions:



Reactants of TiO_2 , B_2O_3 , Al , Mg , Ti , SiO_2 and BaO in the form of powders were used. They all had a particle size < 45 μm except for the BaO which had a particle size < 149 μm . The reactants were first mixed thoroughly by ball milling and green pellets with desired densities were then formed. Two kinds of pellets were fabricated to study the combustion synthesis characteristics. The first had a cylindrical geometry with a diameter of 12.7 mm (0.5 inches) and a mass of 2-3 grams (here it is referred to as a small cylindrical pellet, or SCP) and the second had a spherical geometry with an outside maximum diameter of about 50.8mm (2 inches) and a mass of 55-70 grams (here it is referred to as a

large spherical pellet or LSP). Samples to be used on ISS will be LSP. Figure 1 shows photographs of the LSP green pellets and a reacted product. For the SCP samples, they were ignited at the bottom by a flat W-coil. For the LSP samples, they were ignited from the center by inserting a spiral W-coil into the through-hole (diameter of 14mm, or 0.55 inches) which is shown in Figure 1.

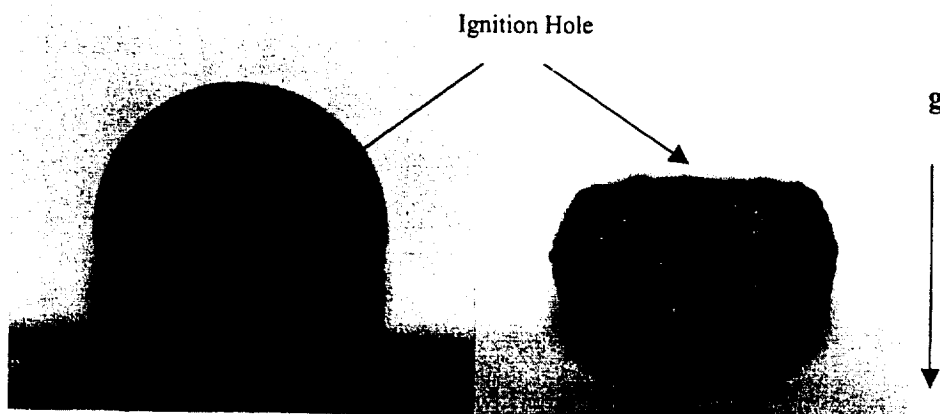


Figure 1 Photographs of a spherical green pellet (left) and the same pellet after combustion synthesis (right). The green pellet had a density of 35%. The composition is $50\text{Al}_2\text{O}_3\text{-}30\text{CaO-}10\text{SiO}_2\text{-}10\text{BaO}$ (wt.%).

All combustion synthesis reactions were conducted in an ultra-high-purity argon atmosphere. For SCP samples, ignition of the combustion reactions was achieved by using a Xantrex power supply (model no XFR40-70) with a computer-controlled power input into the ignition coil. For the LSP samples, the ignition was realized by passing an electrical power from a battery system. One of the advantages of this current set-up is that the ignition power is controlled precisely, therefore exactly the same amount of pre-heating is applied to the green pellet before ignition for green pellets with the same characteristics. This is considered to be crucial in obtaining data of combustion characteristics with high reliability and repeatability. Temperature profiles during the combustion reactions were recorded by a data acquisition system using the DaqPad-1200 from the National Instruments. Two C-type thermocouples (W-5%Re/W-26%Re) were used for the SCP samples while total of five was used for the LSP burns. These five thermocouples were placed at different locations and/or depths of the spherical pellet. A pressure sensor was used to measure the pressure change during the whole process. Finally, a video recording system, consisting of a colour CCD camera with micro-zoom lens combined with a VCR and a digital camera was used to record the whole combustion process. This recording was used to determine the combustion wave velocity.

Samples used for the KC-135 flights were SCP samples. A dedicated payload has been developed to conduct Combustion Synthesis of Advanced Materials (COSYM) under both terrestrial and reduced gravity conditions [6]. The payload includes all of the features described above plus acquisition of gravitational acceleration in three directions during the parabola flights.

Combustion Characteristics and Microstructures

Parameters of combustion characteristics determined were ignition energy, combustion temperature, and combustion wave velocity and selected results are shown in Table 1. The ignition energy (E) data shown in the Table 1 were the amount of energy used to achieve ignition for the current set-up and experimental conditions. Note the total energy to achieve ignition is at the same order of magnitude for both SCP and LSP samples. Since the mass of the LSP samples was about 25 times larger, the energy required for ignition per unit mass was much less for the LSP samples. This was due to the fact that the heat loss for the LSP samples was much less due to the center ignition.

Once the ignition was established, a self-propagating combustion wave propagated toward the unreacted part of the pellet, as shown by a series of images in Figure 2 for a SCP sample. The combustion wave propagated along the longitudinal direction and the combustion wave velocities presented in Table 1 were average linear velocities along this direction. A typical temperature profile for such a SCP sample with a matrix composition (excluding the TiB_2 phase) of

56.9B₂O₃-26.4MgO16.7Al₂O₃ (wt.%) is shown in Figure 3 and can be divided into four regions. The first region (I) represents the temperature of the unreacted part. As the combustion reaction was initiated and began propagating, it also preheated the unreacted portion of the green pellet, forming a preheat zone (Region II). Note that the temperature dropped after reaching the maximum, which is clearly an indication of melting of reactants (B₂O₃ first, then Mg, followed by Al). The molten reactants wet and spread over the TiO₂ particles and the reduction reaction of B₂O₃ and TiO₂ by Al and Mg followed soon after. This lead to the Region III which was the combustion synthesis process. This is the process which forms phases of product. This region is also much narrower than the preheat zone. The fourth region (IV) represents the cooling of the glass melt.

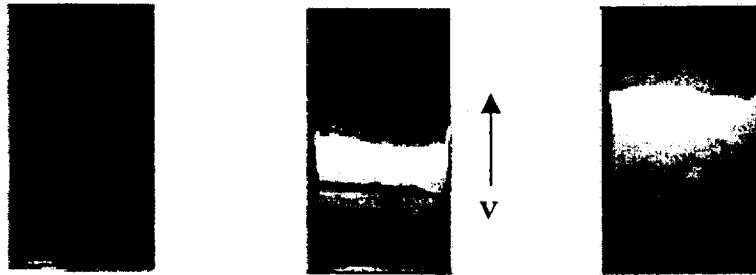


Figure 2 Images of combustion waves for a SCP sample with a green density of 35% and a matrix composition of 41.3B₂O₃-20.9MgO-37.8Al₂O₃ (wt.%)

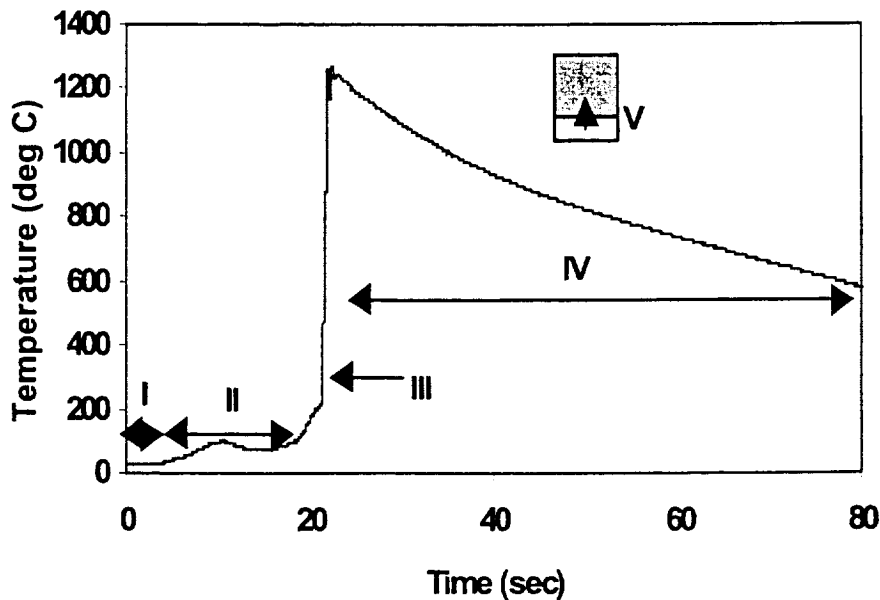


Figure 3 A typical temperature profile during the combustion synthesis of a SCP sample with the matrix composition of 56.9B₂O₃-26.4MgO-16.7Al₂O₃ (wt.%).

Images of a typical LSP sample are shown in Figure 4. After the ignition, the combustion wave propagated along the radial direction initially until it reached the surface near the center hole then propagated along the surface meeting the original combustion wave. The velocity data for the LSP samples presented in Table 1 were determined from total time of burning. Typical temperature profiles for a LSP sample with a matrix composition of 50Al₂O₃-30CaO-10SiO₂-10BaO (wt.%) are shown in Figure 5. The cooling rate was slower than the SCP samples due to the larger mass. Five thermocouples had been used to measure the temperature profiles at different locations of the spherical pellet and it is obvious from Figure 5 that the cooling rates were larger near the surface of the pellet, and smallest near the location where the sample was supported on (T1).

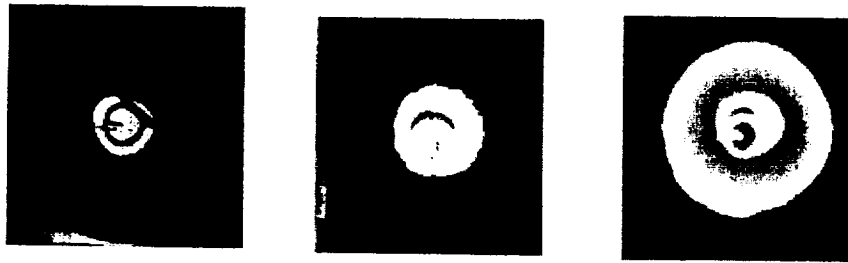


Figure 4 Images of combustion waves for a LSP sample with a green density of 35% and a matrix composition of $41.3\text{B}_2\text{O}_3\text{-}20.9\text{MgO-}37.8\text{Al}_2\text{O}_3$

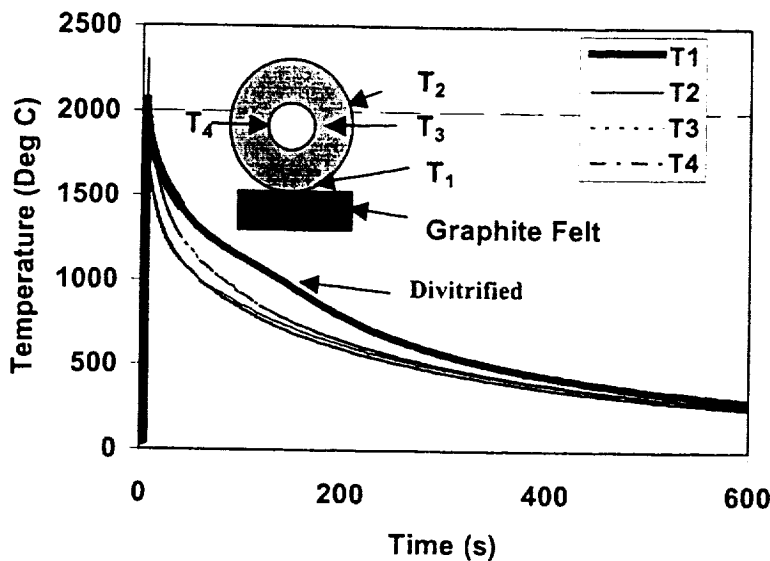


Figure 5
Typical
temperature
profiles during
the combustion
synthesis of a
sample with the
matrix
composition of
 $50\text{Al}_2\text{O}_3\text{-}30\text{CaO-}10\text{SiO}_2\text{-}10\text{BaO}$ (wt.%).

It was found that combustion characteristics of both systems depend highly on the compositions. The higher the aluminium and magnesium oxide content, the higher the combustion temperature and combustion wave velocity due to increased exothermicity of the reactions. It was also found that the combustion characteristics of System 1 were highly dependent on the green density of pellets. As the density of green pellets increased, both the combustion temperature and wave velocity decreased. For System 2, the combustion characteristics were much less dependent on the green density of pellets. The data shown in Table 1 were from pellets with a green density of about 35%. Using a low green density pellet (~35%) was particularly important for compositions that had a lower exothermicity. For instance, for samples with a matrix composition containing less than 20 mol.% Al_2O_3 for System 1, a self-propagating combustion reaction wave could not be generated for the samples with a green density of 60%. However, successful ignitions were achieved for most samples with a green density around 35%. Apparently, these pellets with 35% green density had less heat loss due to conduction than those with 60% green density. Munir [8] suggested that the adiabatic temperature (T_{ad}) for SHS reactions must be higher than 1800K. The adiabatic temperature for the $56.9\text{B}_2\text{O}_3\text{-}26.4\text{MgO-}16.7\text{Al}_2\text{O}_3$ (Matrix) was only 1566K and SHS reactions were still obtained for most SCP samples with a green density of 35% (some also quenched out during propagation). For the LSP samples, all pellets with 35% green density could be ignited and reacted to completion without any difficulty, which was most likely due to the fact that the center-ignited spherical samples reacted closest to the adiabatic condition with minimum possible heat loss. This conclusion is supported by the fact that both the combustion temperature and wave velocity for the LSP samples were higher than SCP samples, as shown in Table 1.

Table 1 Combustion Characteristics for SCP and LSP Samples

Compositions [†] (w t . %)	T _{ad} (K)	Pellet	E (J)	T _c (K)	V (mm/s)	Microstructures [†]
41.3B ₂ O ₃ -20.9MgO -37.8Al ₂ O ₃	2017	SCP	1348±139	1802±38	2.3±0.2	Pure Glass
		LSP	1846±76	1808±31	> 4.2	Divitrified in Center
56.9B ₂ O ₃ -26.4MgO -16.7Al ₂ O ₃	1566	SCP [‡]	1462±100	1509±92	1.1±0.2	Pure Glass
		LSP	2 4 5 7	1566±25	> 1.6	Slightly Divitrified
50Al ₂ O ₃ -30CaO- 10SiO ₂ -10BaO	-	SCP	1210±207	2306±142	4.3±0.1	Mainly Glass
		LSP	1837±94	2570±46	> 5.1	More Divitrified Phases
45Al ₂ O ₃ -35CaO- 10SiO ₂ -10BaO	-	SCP	1260±28	2050±175	1.4±0.4	Divitrified
		LSP	1603±105	2487±110	> 3.6	Divitrified

† Matrix Phases only (Excluding TiB₂). ‡ Data were from samples that achieved ignition.

The glass-forming compositions have been identified using X-ray Diffraction (XRD) and microscopes and results are also presented in Table 1. For the System 1, it was found that with the increase of B₂O₃, more glass phase was formed since B₂O₃ is a glass-former. However, the maximum amount of B₂O₃ was found to be around 60 mol%, beyond which a self-propagating combustion reaction could not be generated. Examples of the XRD patterns and photomicrographs of samples from System 1 with and without divitrification are shown in Figures 6 and 7.

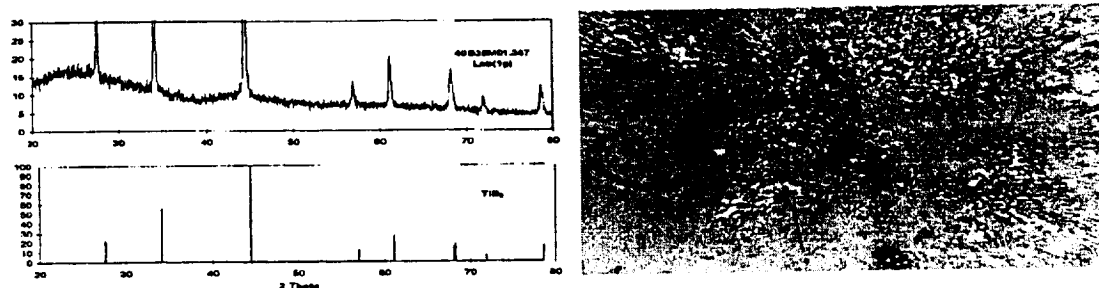


Figure 6 The XRD Patterns and Optical photomicrograph of a SCP sample with a matrix composition of 41.3B₂O₃-20.9MgO-37.8Al₂O₃ (wt.%) reacted at 1-g in laboratory

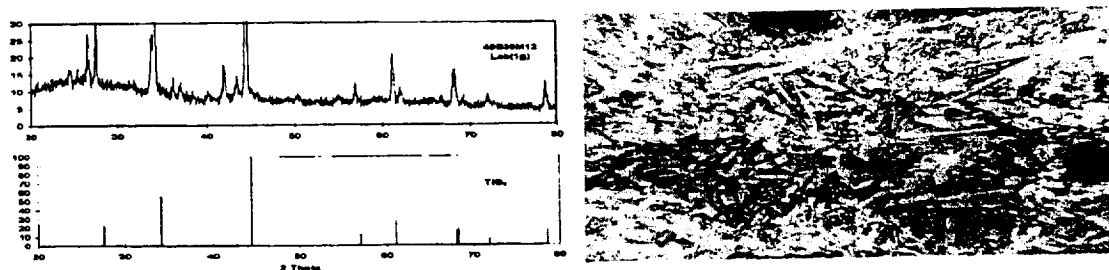


Figure 7 The XRD Patterns and Optical photomicrograph of a SCP sample with a matrix composition of 39.5B₂O₃-17.1MgO-43.4Al₂O₃ (wt.%) sample reacted at 1-g in laboratory

For System 2, the amount of glass phases increased with the initial increase of the SiO₂. This is due to the silicon dioxide being a glass-former, which promotes change of coordination of cation ions (Al³⁺) from 6 to 4 and formation of a three dimensional glass network. However, enhanced divitrification occurred when the SiO₂ content was over 20 wt.%, which is believed to be caused by the fact that the combustion temperatures were too low to melt the SiO₂ uniformly [5]. The role that the BaO plays on the glass formation is less clear. In the present work, it was found that the addition of BaO reduced the viscosity of the glass melt (SiO₂ had the opposite effect) and that adequate amount of both SiO₂ and BaO is required to form a pure glass matrix. For the LSP samples, it was found that the microstructure was less uniform than that of SCP samples and more divitrification was observed at the center of spherical sample than

at the surface where the cooling rate was faster. Enhanced divitrification was observed at the area of support (i.e., container effect, see later). The ceramic phase TiB_2 , which formed as a by-product as shown in Reactions (1) and (2) in both glass systems has a particulate morphology with the size less than $1\mu\text{m}$.

Effects of Gravity

The effects of gravity on the combustion synthesis of various materials were studied before. Samples produced at reduced gravity had more uniform microstructure [9, 10], high porosity [11,12], and difference in combustion characteristics [9, 13, 14]. The current study was conducted onboard of the KC-135 at the Johnson Space Center in Houston and selected results are presented in Table 2. For the two compositions from System 1, the green density of the pellets was ~35% while the green pellets for the two compositions of System 2 were fabricated to about 60% of their theoretical densities. The data shown in Table 2 seems to suggest that gravity had little effect on both the combustion temperature and wave velocity for the two compositions from System 1. On the other hand, the combustion wave velocity seemed to be lower at reduced gravity for the two compositions from System 2. Some studies on combustion synthesis of crystalline materials also found that the combustion temperatures were lower under reduced gravity conditions [9, 13]. In addition, the width of the combustion wave front (D) was larger for samples reacted under reduced gravity. These findings may indicate that gravity had a larger effect on those samples that had higher thermal conductivity.

Substantial sedimentation of samples occurred during the combustion synthesis process (Figure 1) due to formation of liquid. The effect of gravity on the microstructure seemed to be more significant than on the combustion characteristics. Low gravity seems to promote vitrification for some compositions and an example is shown in Figure 8. However, more divitrification occurred for samples of System 1 reacted under reduced gravity conditions, caused by the fact that the 20 seconds of typical reduced gravity in a parabola was not long enough to solidify the glass melts for the system which had a melting temperature typically below 650°C [14].

Table 2 Effects of Gravity on Combustion Characteristics and Microstructures

Compositions [†] (wt%)	G's	E (J)	D (mm)	Tc (K)	V (mm/s)	Microstructures
41.3B ₂ O ₃ -20.9MgO-37.8Al ₂ O ₃	Low	1335±25	0.94±0.12	1746±95	2.9±0.1	Slightly Divitrified
	1-g	1291±23	0.50±0.08	1665±60	1.8±0.1	Pure Glass
47.63B ₂ O ₃ -21.4MgO-31.0Al ₂ O ₃	Low	1332±19	1.1±0.13	1675±79	1.6±0.2	Pure Glass
	1-g	1287±21	0.80±0.12	1796±20	2.6±0.3	Pure Glass
50Al ₂ O ₃ -30CaO-10SiO ₂ -10BaO	Low	1991±451	0.96±0.14	2199±317	4.5±0.2	Mainly Glass
	1-g	1560±31	0.75±0.06	2158±113	5.2±0.3	Slightly Divitrified
44Al ₂ O ₃ -35CaO-10SiO ₂ -10BaO	Low	2399±57	1.49±0.16	2182±84	3.8±1.2	Divitrified
	1-g	1569±11	1.00±0.15	2158±113	4.6±0.3	Divitrified

[†] Matrix Phases only (excluding TiB_2).

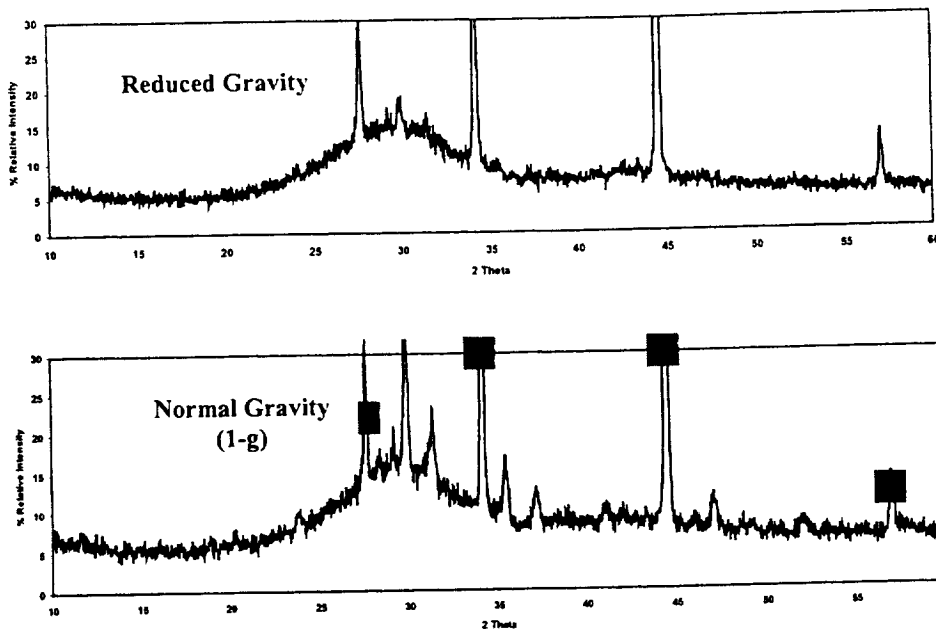


Figure 8 The XRD patterns for SCP samples with a matrix composition of $50\text{Al}_2\text{O}_3$ - 30CaO - 10SiO_2 - 10BaO (wt.%) reacted under reduced gravity and normal (1-g) gravity conditions (The Square symbols: TiB_2).

Containerless Combustion Synthesis (CCS) of Glasses

Generally speaking, when high-purity glasses are required, containerless processing is preferred since contamination from the container as a result of high temperature reaction between the container and the glass melt is totally eliminated. When the glasses are produced by the SHS technique as in the present work, containerless combustion synthesis (CCS) is also critical in three aspects. First of all, the CCS approach eliminates heat loss by thermal conduction which makes production of certain low exothermic combustion compositions possible. Secondly, contamination by container is also eliminated since the combustion temperature is usually much higher than the temperature used in the traditional melting furnace. For instance, to produce the same calcium aluminide glasses using a furnace requires melting at 1550°C for hours but in the CCS technique, the combustion temperature was much higher making it more reactive with container walls. Finally, the CCS makes production of homogeneous compositions possible. This can be illustrated by Figure 9 which shows a photograph of the area that sat on the graphite felt during the combustion synthesis process. Clearly, the microstructure of this part is different from the rest and more divitrification occurred. This conclusion is also supported by the temperature profile (T1) shown in Figure 5 where it can be seen that enhanced divitrification occurred in this area. In the present work, it was also found that the area of support was unreacted for pellets with low exothermicity and relatively high thermal conductivity.

In previous studies on microgravity containerless glass processing, a traditional melting/fusion technique was used and the samples that were produced were all very small in mass regardless of the levitation technique being employed. In the current work, the two glass systems will be produced containerless on ISS using Space-DRUMSTM [15,16]. The mass of samples will be 55-70 grams.

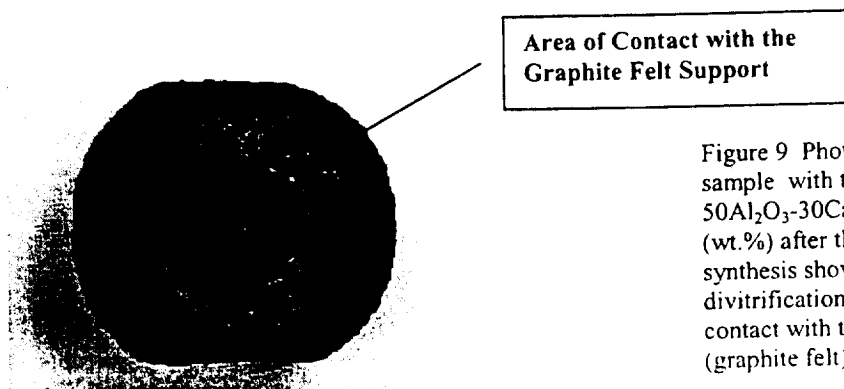


Figure 9 Photograph of a LSP sample with the compositions of $50\text{Al}_2\text{O}_3$ - 30CaO - 10SiO_2 - 10BaO (wt.%) after the combustion synthesis showing more divitrification at the part in contact with the support (graphite felt).

